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Technical Note

Levitating Droplet Electroanalysis

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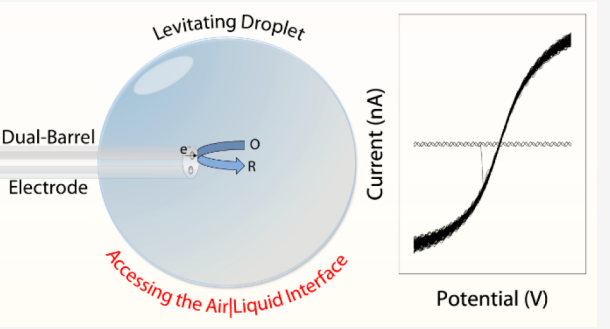
ABSTRACT: Chemical reactions that occur in droplets proceed much differently compared to bulk phases. For instance, many groups have studied droplets during levitation by mass spectrometry and fluorescence to gain more detailed mechanistic insight. Such droplets maximize the probability of solution species interacting with the solution−air interface, an interface that is inherently difficult to probe electrochemically. In this Technical Note, we overcome this limitation by developing a laser-pulled dual-barrel electrode. Having two microwires sealed within the same glass capillary allows one to make two-electrode measurements. We show that the electrode can be positioned within a levitating water droplet and that the voltammetry of a redox indicator (hexacyanoferrate (II/III)) can be observed in real-time. Such foundational measurement tools are important to probe a variety of chemical reactions at complex interfaces.



The study of the air|liquid interface has become an intriguing avenue of inquiry for analytical chemists in recent years. Specifically, droplets in air present a unique opportunity to study the air|liquid interface, owing to their large surface:volume ratio.[1,2] Studies of microdroplets in air are typically performed with ensemble measurements of electrospray or nebulized droplets. Cooks[3−6] and Zare[7,8] have used these methods to quantify reaction acceleration and study the species which may be responsible for the observed reaction acceleration. While these measurements can be useful for gaining insight into the air/liquid interface, the study of individual droplets in air would offer a more controlled experimental environment. As such, groups have turned toward acoustic levitation for measurements of single droplets in air. Volmer[9−12] and Beauchamp[13] have reported several studies of real-time reaction monitoring in levitating droplets via mass spectrometry, allowing for characterization of reactions spanning from small molecules to lipids and peptides.

Here, we provide a novel electrochemical method for studying a single droplet in air. While our lab has used electrochemical methods to study liquid aerosols[14−16] and enzymatic reaction acceleration in microdroplets in oil,[17] our methods for studying droplet suspended in air have involved the bombardment of the electrode surface with droplets and have not allowed for the study of single microdroplets. Recently, we have become more interested in developing robust electroanalytical tools to probe the droplet|air interface.[18] Using an acoustic levitator to levitate an aqueous droplet (~3 μL) and a laser-pulled dual-barrel electrode, we are able to perform cyclic voltammetry of a well-behaved redox couple, hexacyanoferrate (II/III), directly within a single levitating droplet. Importantly, we demonstrate that the probe can be inserted and removed without perturbing the levitated droplet. This method represents a containerless approach to electrochemistry and a unique approach to the study of droplets in air.

EXPERIMENTAL SECTION

To probe a single droplet via electrochemistry, a complete electrochemical cell must be able to penetrate the droplet without significant droplet movement or wetting of the electrode. A more detailed materials and methods section can be found in the Supporting Information. A laser-pulled dual-barrel electrode was fabricated and used to facilitate this measurement. This electrode was fabricated by laser-pulling a quartz theta capillary, where both channels were threaded with platinum (Pt) wire (d = 25 μm), with a Sutter P-2000 laser puller. The specific pulling parameters can be found in the Supporting Information. We also note that pulling parameters vary greatly based on laboratory, humidity, and many other factors, and we have recently published a troubleshooting guide for laser-pulling electrodes.[19] Electrical connection was made to the pulled electrode by inserting stripped electrical wire coated with gallium into each barrel and securing the wires in place with hot glue. The pulled electrode was then polished with a micropipet beveler (Sutter BV-10) and characterized optically with a Leica DM750 M standing

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microscope and electrochemically by cyclic voltammetry in 5 mM hexacyanoferrate (II/III) in 1 M potassium chloride (KCl) (Figure 1). Optical microscopy revealed that the

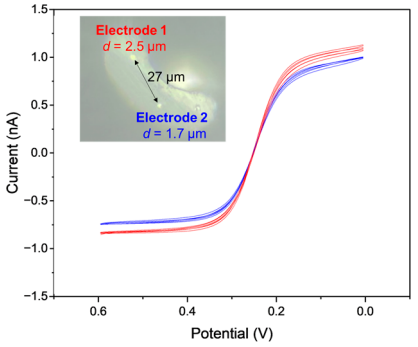


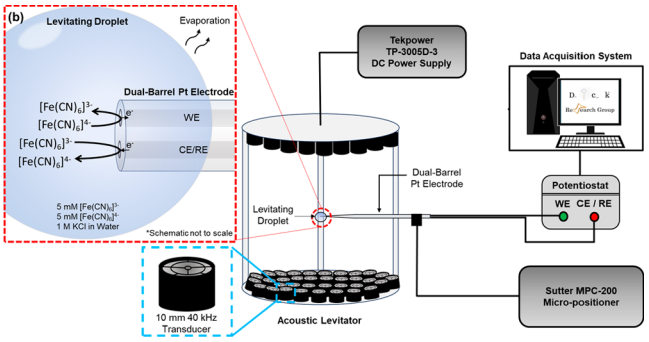
Figure 1. Cyclic voltammetry of 5 mM hexacyanoferrate (II/III) in 1 M KCl taken on a fabricated dual-barrel Pt electrode. Each voltammogram was taken with one designated electrode as the working electrode, a commercial CHI Ag/AgCl reference electrode, and a Pt wire counter electrode (d = 0.5 mm) from 0.6 to 0 V at a scan rate of 10 mV/s over 3 scans after an applied quiet time of 2 s. An optical microscopy image of the electrode surface with measured electrode diameters and distance between each electrode is provided in the inset. Voltammetry is presented by polarographic convention.

diameters for the working and counter/reference electrode were 1.7 and 2.5 μm, respectively, and they were 27 μm apart. Because the counter/reference electrode is on the same order of size as the working electrode, special care must be taken to be quantitative with respect to half-wave potentials, uncompensated resistance, and rigorous quantification of kinetic parameters.

For the electrochemical characterization, each electrode was used as a working electrode against a commercial CHI Ag/AgCl reference and a Pt wire (d = 0.5 mm) counter electrode. Voltammetry was in 5 mM hexacyanoferrate (II/III) in 1 M KCl from 0.6 to 0 V at a scan rate of 10 mV/s over 3 scans after an applied quiet time of 2 s. After electrode characterization, the electrode which was determined to be the larger electrode (Electrode 1) was used as the quasi-reference counter electrode, and the smaller electrode (Electrode 2) was used as the working electrode for all further experiments. The electrode was then treated with dichlorodimethyl silane to render the glass hydrophobic and prevent the levitated droplet from wetting the probe. To accomplish this, the dual-barrel electrode was dipped in 5 mL of the silane solution in a scintillation vial for 5 s. Afterward, the electrode was rinsed well with acetone and Milli-Q water. The treated electrode was then used to perform cyclic voltammetry in 5 mM hexacyanoferrate (II/III) in 1 M KCl bulk solution with the configuration outlined above as shown in Figure S1. This voltammetry was performed from 0.6 to −0.5 V at a scan rate of 10 mV/s.

After a suitable dual-barrel electrode was fabricated and characterized, the experimental setup (Scheme 1) was assembled. A photograph of the actual experimental setup can be seen in Figure S2. An acoustic levitator kit was purchased from Maker Fabs and was constructed for droplet levitation.[20] The constructed levitator was connected to a Tekpower TP-3005D-3 DC Power Supply, and an applied voltage of 16 V (with an output current of 0.75 A) was used to levitate a 3 μL droplet of 5 mM hexacyanoferrate (II/III) in 1

Scheme 1. Experimental Setup with (b) Schematic of the Electrochemical Measurement within the Levitated Droplet



M KCl. It should be noted that while a 3 μL droplet was used in this work, droplets ranging from 1.3 to 18 μL could be easily levitated with this system. We could also levitate smaller droplets; however, the interrogation of smaller droplets depends on our ability to miniaturize the electrode probes. After the droplet was levitated, the dual-barrel electrode was attached to a Sutter MPC-200 micropositioner, and the wire connected to Electrode 2 was connected to the working electrode lead while the wire connected to Electrode 1 was connected to the counter/reference electrode leads of a CHI 601E potentiostat. The electrode was then inserted into the levitating droplet using the micropositioner and a USB digital microscope (50× magnification) was used to help visualize the electrode placement. It should be noted that the electrode needed to be perfectly horizontal and centered within the droplet to be successfully inserted. Voltammetry and digital microscopy videos taken during the electrode insertion and removal process and can be seen in Figure S3/Supplementary Video 1 and Figure S4/Supplementary Video 2, respectively.

Figure 2 shows images of the electrode and levitating droplet before (Figure 2A) and after (Figure 2C) insertion along with the correlated scans from the voltammetry taken over the course of the experiment (Figure S3). Before the electrode is inserted into the droplet, there is no significant measured current (Figure 2B). Once the electrode is inserted into the droplet, a sudden increase in current, followed by the characteristic voltammetric response of hexacyanoferrate (II/II) can be seen (Figure 2D). The half-wave potential is centered around 0 V because the counter/reference electrode is poised by the hexacyanoferrate (II/III) couple. Over the time course of the experiment (approximately 3 min), the limiting current increases slightly. This is likely due to evaporation of the levitating droplet. Droplet evaporation is also likely responsible for a smaller droplet radius than anticipated for a 3 μL droplet. Additionally, the limiting current observed in the levitating droplet (~1.7 nA) is more than twice the limiting current observed with the same electrode configuration in bulk solution (~0.75 nA; Figure S1). This increase in limiting current is most likely due to the convection induced from the acoustic levitation of the droplet.[21] Figure 2E shows the electrode and droplet after the electrode was removed from the droplet, showing that the removal process does not significantly perturb the droplet.

Here, we have presented a rather simple and robust method for electrochemical measurement in a single acoustically levitated droplet. We have demonstrated the ability to monitor a well-behaved redox mediator in real-time. For the purposes of this Technical Note, we have reported only on this single

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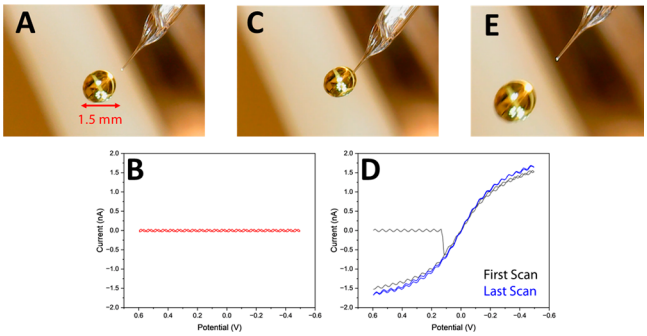

Figure 2. (A and C) Optical micrographs of the levitating droplet and the dual-barrel electrode taken with a USB microscope before (A) and after (C) the electrode was placed inside the droplet. (B and D) Cyclic voltammetry in a levitating 3 μL droplet of 5 mM hexacyanoferrate (II/III) in 1 M KCl taken with the dual-barrel electrode. Electrode 2 (d = 1.7 μm) was used as the working electrode and electrode 1 (d = 2.5 μm) was used as the quasi-reference counter electrode. Voltammetry was taken from 0.6 to −0.5 V at a scan rate of 500 mV/s scans after a quiet time of 2 s. (B) CV scans taken before and while (D) the electrode was inserted into the droplet. The first scan (black trace) was the first scan taken after the electrode entered the droplet, and the last scan (red trace) was taken 200 s after the initial insertion. Voltammetry is presented in polarographic convention. (E) Optical micrograph of the levitating droplet and the dual-barrel electrode taken with a USB microscope after the electrode was removed from the droplet. This micrograph was taken at a slightly larger magnification than in panels A and C.

model system as a proof-of-concept for the presented method. This method presents an exciting avenue for studying single droplets in air and ultimately the air|liquid interface. Currently, the presented method is limited to large droplets (1.3−18 μL). This limitation is not only a function of the levitator used but also the electrode probe, where a droplet must be large enough to house the probe. In this work, the electrode tip is ∼30 μm in diameter, but the electrode pulling parameters could be optimized to miniaturize this tip further to mitigate this limitation. Our presented technique is a step toward accessing the liquid|air interface using electrochemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.3c04123.

Extended materials and methods, dual-barrel electrode laser-puling parameters, CV of bulk hexacyanoferrate (II/III) solution taken with fabricated dual-barrel electrode, photograph of experimental setup, and CV measurements taken during electrode insertion and removal (PDF)

Supplementary Video 1: Video of electrode insertion into levitating droplet (MP4)

Supplementary Video 2: Video of electrode removal from levitating droplet (MP4)

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Author Contributions

L.E.K. fabricated and characterized the dual-barrel electrode. L.E.K. and L.Q. performed levitating droplet experiments. The manuscript was written through contributions of all authors. J.E.D. supervised all aspects of the research presented. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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